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(57) Abstract

Colored particulate compositions comprising an inner core having a color body distributed on a particulate carrier, and two discrete coatings of water–soluble dextrin glue on said inner core. The compositions are useful as speckles in cleaning products, especially laundry bars, having a contrasting background color. Also disclosed is a process for preparing said colored particulate compositions.

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COLORED PARTICULATE COMPOSITIONS

FIELD OF THE INVENTION

The present invention relates to colored particulate compositions which are especially useful for imparting decorative color contrast to laundry bars.

BACKGROUND OF THE INVENTION

Synthetic laundry bars typically comprise an anionic surfactant such as the alkali metal salt of an alkylbenzene sulfonic acid or alkali metal salt of an alkyl sulfate and one or more alkaline builders such as alkali metal polyphosphates, carbonates or silicates. Experience has shown that the attractiveness of laundry bars to consumers is enhanced when such products contain particles (speckles) which differ in color from the basic (i.e. background color) of the product. Aside from purely aesthetic purposes, the speckles can also be used as a vehicle for performance enhancing ingredients such as fabric substantive blueing, bleaches, fabric softeners, optical brighteners, etc. The combination of color and a particular performance-enhancing ingredient can be used to reinforce the advertising message which is used to promote the product to the consumer.

One problem frequently encountered in manufacture and/or storage of speckled products is maintenance of the color integrity of the speckle, i.e. the dye or pigment in the speckle can diffuse into the product, thereby causing a smeary appearance rather than one of sharply defined color bodies on a contrasting background.

SUMMARY OF THE INVENTION

The present invention is directed to colored particulate compositions which maintain their color integrity when dispersed in a product having a contrasting color. The invention also ncompasses detergent products, in particular laundry bars, containing said particulat compositions and a process for preparing the colored particles.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention it has been found that by applying two discrete coatings (i.e. layers) of a water soluble glue onto colored particles of materials suitable for use in detergent products, colored particulate compositions are obtained which maintain their color integrity when dispersed in a laundry bar product, but which easily and quickly disintegrate and dissolve/disperse into the aqueous medium used by the consumer for laundering fabrics. The colored particulate compositions herein comprise from about 50% to about 95% preferably (70% to about 85%) particulate carrier, from about 1% to about 30% (preferably 5% to about 7%) color body, from 1% to about 40% (preferably 5% to about 15%) dextrin in the form of dextrin glue, wherein from about 5% to about 85% (preferably from about 30% to about 70%) of the dextrin comprises the first (inner) coating and the balance of the dextrin comprises the second (outer) coating, and from about 0.3% to about 35% total moisture. All percentages, proportions and ratios set forth herein are by weight unless specified otherwise.

Particle Components

a) Particulate carrier

The particulate carrier serves as a substrate and diluent for the color body (i.e. dye or pigment) to be used in the colored particle. It can be any water soluble or water dispersible, hydratable or non-hydratable, particulate material which is suitable for use in detergent products. It can be an essentially performance-neutral material such as sodium sulfate, but preferably it is a material, or combination of materials, which contributes to or enhances the laundry performance of the product. Examples of performance-related materials are bleaches, e.g. sodium perborate or sodium percarbonate, detergency builders, e.g. sodium tripolyphosphate, sodium carbonate, magnesium sulfate, zeolite, etc. Combinations of particulate carrier materials can be used. A more detailed description of detergent materials, with particular reference to formulation of laundry detergent bars is set forth hereinafter.

The particulate detergent material used as the carrier for the color body in the glue coated particles of the instant invention is in the form of a powder, typically having a particle size of from about 1650 to about 45, preferably from

about 415 to about 150 microns. These powder particles become agglomerated in the process of preparing the colored particles of the invention.

b) Color bodies

The color bodies used in the particles of the present invention can be any colored materials (typically dyes or pigments) which are useful to impart the desired visual effects to the products in which the particles are to be used. The color body can be substantive or non- substantive to fabrics, depending on whether it is desired to impart color to fabrics on which the product is used. The imparting of a blue tint to fabrics is often desired, and for this purpose substantive dyes such as Pigmasol or pigments such as ultramarine blue pigment can be used. Examples of non-substantive dyes which can be used are D&C Yellow No.10, supplied by Warner Jenkenson, USA; D&C Yellow No.11 supplied by Hilton Davis, USA; FD&C Blue No. 1, supplied by Warner Jenkenson, USA; and the various phthalocyanine dyes supplied by Hilton Davis, USA.

In preparing the colored particulate compositions of the invention the color bodies are dissolved/dispersed in water , typically at a concentration of from about 0.1% to about 80% (preferably 2% to 65%), based on weight of dye slurry/dispersion, and sprayed onto the particulate carrier.

c) Glue

The water soluble dextrin glue composition used herein serves to coat the colored particles and prevent dispersion of the color body into the rest of the detergent bar product until it is used in an aqueous medium. It is present on the particle in the form of two discrete coatings. The combined coatings (based on weight of dextrin) comprise from about 5% to about 50% of the particle. From about 5% to about 85% of the total amount of the dextrin is in the inner coating and the remainder is in the outer coating.

The water soluble dextrin glue used in the present invention is prepared by cooking a solution/dispersion of from about 5% to about 80% (preferably 20% to 35%) dextrin in water.

In addition to dextrin, the glue composition used herein can contain small amounts of additives. For example, carboxymethyl cellulose and/or other soil suspending agents described hereinafter, can be added to minimize any fabric staining by the color body. These agents can be added as part of the dextrin glue composition, as part of the color body solution/dispersion, or both. When

used, soil suspending agents are added in an amount so as to provide from about 0.1% to about 10% in the final colored particulate composition. Sodium tetraborate decahydrate or pentahydrate at levels of from 1% to about 100% (based on weight of dextrin) can be included to increase glue viscosity/tackiness, raise glue pH, and speed up the drying of the glue coating on the colored particles.

The colored particles herein contain from about 0.3% to about 35% total moisture, i.e. free moisture and any moisture of hydration. Total moisture can be determined by oven drying at 105°C for one hour. Free moisture can be determined by differential scanning calorimetry and will typically be in the range of from 0% to 5%.

Laundry Bars

The colored particles of the present invention are particularly suitable for use in synthetic laundry bars, although they can suitably be used in oth r cleaning products such as laundry granules, granular hard surface cleaners, and toilet bars. The colored particles are typically used in laundry bars at levels of from about 0.01% % to about 15%.

Synthetic laundry bars typically comprise an anionic synthetic surfactant and an alkaline detergency builder. Various other ingredients are typically also present to enhance cleaning performance and/or to impart other desirable characteristics to fabrics.

Anionic surfactants which are suitable for use in laundry bars include the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_{8-18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branch d chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable sulfonates are linear straight chain alkylbenzene sulfonates in which the average

number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11-13} LAS. The alkali metal salts, particularly the sodium salts of these surfactants are preferred.

Other suitable anionic synthetic surfactants are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

In addition, suitable anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred anionic surfactants are C_{10-18} alkyl sulfates and C_{10-18} alkylbenzene sulfonates, and mixtures thereof.

The amount of anionic synthetic surfactant typically used in laundry bars is from about 4% to about 30%, preferably from about 6% to about 20%.

Fatty acid soaps are often used in combination with synthetic surfactants in synthetic laundry bars. Suitable soaps are the water soluble salts of fatty acids having from about 8 to about 22 carbon atoms in their alkyl chains. these include the alkali metal soaps such as sodium and potassium as well as the ammonium and alkylolammonium salts of the fatty acids. Preferred soaps are the alkali metal (especially sodium) salts of fatty acids having from about 12 to about 18 carbon atoms in their alkyl chains. These are typically the soaps derived from coconut and tallow fatty acids. Soaps, when used, are typically present at levels up to 50%, preferably 10% to 35%.

Other types of surfactants suitable for use in the granular detergent compositions of step (a) includes nonionic, cationic ampholytic, and zwitterionic types.

Typical nonionic surfactants include the alkylene oxide condensates of hydrocarbyl groups (e.g. alkyl or alkyl phenyl) wherein the hydrocarbyl groups contain from about 8 to about 22 carbon atoms. Nonionics also include semi polar compounds such as C_8-C_{22} amine oxides. An extensive discussion of nonionic surfactants is found in U.S. Pat. 5,338,491 Conner, et al issued August 16, 1994. Nonionics also include fatty acid amide surfactants of the formula

$$R_2 - \overset{O}{\overset{\|}{C}} - \overset{R_1}{\overset{|}{N}} - Z$$

wherein: R_1 is H, C_1-C_8 hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C_1-C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5-C_{32} hydrocarbyl moiety, preferably straight chain C_7-C_{19} alkyl or alkenyl, more preferably straight chain C_9-C_{17} alkyl or alkenyl, most preferably straight chain C_{11}-C_{19} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH_2-OH$, $-CH(-CH_2-OH)-(CHOH)_{n-1}-CH_2-OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)-CH_2-OH$, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2-OH$.

In the above formulas, R_1 can be, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, 2-hydroxy ethyl, or 2-hydroxy propyl. For highest sudsing, R_1 is preferably methyl or hydroxyalkyl. If low sudsing is desired, R_1 is

preferably C_2-C_8 alkyl, especially n-propyl, iso-propyl, n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

Specific examples of this type of amide surfactant include C_{12}-N-(3-methyxypropyl) glucamide and coconut n-methyl glucamide. Further disclosure of this type of amide surfactant can be found in U.S. Pat. 5,376,310, Cripe, issued December 27, 1994.

Cationic detersive surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:

$$[R^2(OR^3)_y[R^4(OR^3)_y]_2R^5N^+X^-$$

wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl, ring structures formed by joining the two R4 groups, $CH_2CHOHCHOHCOR6CHOHCH_2OH$ wherein R6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R5 is the same as R4 or is an alkyl chain wherein the total number of carbon atoms of R2 plus R5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Other cationic surfactants useful herein are also described in U.S. Pat. No. 4,228,044, Cambre, issued Oct. 14, 1980. Ampholytic surfactants can b broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Pat. No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants. Zwitterionic surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Pat. No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48 for examples of zwitterionic surfactants.

A further extensive disclosure of various types of surfactants can be found in US Pat. 3,664,961, Norris, issued May 23, 1972.

Builders useful in the laundry bars are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, borates, polyhydroxy sulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above. Preferred for use herein are the phosphates, carbonates, silicates, polycarboxylates, and mixtures thereof. More preferred are sodium tripolyphosphate, tetrasodium pyrophosphate, sodium citrate, sodium tartrate sodium mono- and di-succinates, and mixtures thereof. .

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21,. and orthophosphates. Oth r phosphorus builder compounds are disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,137; 3,400,176 and 3,400,148, all of which are incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrat , and Zeolites such as Zeolite A. Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalonic acid.

Builders generally comprise from about 5% to about 50%, preferably from about 20% to about 40% of detergent bars.

Fabric softening clay is a useful, optional ingredient in laundry bars. The useful clays are smectite-type clays, which can be described as expandable,

three-layer clays; i.e., alumino-silicates and magnesium silicat s, having an ion exchange capacity of at least about 50 meq/100 g. of clay. Preferably the clay particles are of a size that they can not be perceived tactilely, so as not to have a gritty feel on the treated fabric of the clothes. The fabric softening clay can be added to the bar to provide about 1% to about 30% by weight of the bar, more preferably from about 5% to about 20%, and most preferably about 8% to 14%.

It has been found that the use of a clay flocculating agent in a laundry bar containing softening clay provides surprisingly improved softening clay deposition onto the clothes and clothes softening performance, compared to that of laundry bars comprising softening clay alone. The polymeric clay flocculating agent is selected to provide improved deposition of the fabric softening clay. Typically such materials have a high molecular weight, greater than about 100,000. Examples of such materials can include long chain polymers and copolymers derived from monomers such as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Gums, like guar gums, are suitable as well. The preferred clay flocculating agent is a poly(ethylene oxide) polymer.

A particularly preferred optional component for laundry bars is a detergent chelant. Such chelants are able to sequester and chelate alkali cations (such as sodium, lithium and potassium), alkali metal earth cations (such as magnesium and calcium), and most importantly, heavy metal cations such as iron, manganese, zinc and aluminum. Preferred cations include sodium, magnesium, zinc, and mixtures thereof. The detergent chelant is particularly beneficial for maintaining good cleaning performance and improved surfactant mileage, despite the presence of the softening clay and the clay flocculating agent.

The detergent chelant is preferably a phosphonate chelant, particularly one selected from the group consisting of diethylenetriamine penta(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof, and an acetate chelant, particularly one selected from the group consisting of diethylenetriamine penta(acetic acid), ethylene diamine tetra(acetic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate) di thylenetriamine penta (acetate), and mixtures thereof.

Preferably such salts or complexes have a molar ratio of metal ion to chelant molecule of at least 1:1, preferably at least 2:1.

The detergent chelant can be included in laundry bars at a level up to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.2% to about 2%, most preferably from about 0.5% to about 1.0%. Such detergent chelant component can be used beneficially to improve the surfactant mileage of the present laundry bar, meaning that for a given level of anionic surfactant and level of detergent chelant, equivalent sudsing and cleaning performance can be achieved compared to a similar bar containing a higher level of the anionic surfactant but without the detergent chelant.

Another preferred additional component of laundry bars is fatty alcohol having an alkyl chain of 8 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms. Fatty alcohol is effective at reducing the bar wear rate and smear (mushiness) of laundry bars. A preferred fatty alcohol has an alkyl chain predominantly containing from 16 to 18 carbon atoms, so-called "high-cut fatty alcohol," which can exhibit less base odor of fatty alcohol relative to broad cut fatty alcohols. Typically fatty alcohol is contained in the laundry bar at up to a level of 10%, more preferably from about 0.75% to about 6%, most preferably from about 2% to about 5%. The fatty alcohol is generally added to a laundry bar as free fatty alcohol. However, low levels of fatty alcohol can be introduced into the bars as impurities or as unreacted starting material. For example, laundry bars based on coconut fatty alkyl sulfate can contain, as unreacted starting material, from 0.1% to 3.5%, more typically from 2% to 3%, by weight of free coconut fatty alcohol on a coconut fatty alkyl sulfate basis.

Another preferred optional component in laundry bars is a dye transfer inhibiting (DTI) ingredient to prevent diminishing of color fidelity and intensity in fabrics. A preferred DTI ingredient can include polymeric DTI materials capable of binding fugitive dyes to prevent them from depositing on the fabrics, and decolorization DTI materials capable of decolorizing the fugitives dye by oxidation. An example of a decolorization DTI is hydrogen peroxide or a source of hydrogen peroxide, such as percarbonate or perborate. Non-limiting examples of polymeric DTI materials include polyvinylpyrridine N-oxide, polyvinylpyrrolidone (PVP), PVP-polyvinylimidazole copolymer, and mixtures thereof. Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as "PVPI") ar also pref rred for use herein.

Another preferred optional component in laundry bars is a secondary fabric softener component in addition to the softening clay. Such materials can be used at levels of about 0.1% to 5%, more preferably from 0.3% to 3%, and can include: amines of the formula $R_4R_5R_6N$, wherein R_4 is C_5 to C_{22} hydrocarbyl, R_5 and R_6 are independently C_1 to C_{10} hydrocarbyl. One preferred amine is ditallowmethyl amine; complexes of such amines with fatty acid of the formula R_7C00H, wherein R_7 is C_9 to C_{22} hydrocarbyl, as disclos d in EP No. 0,133,804; complexes of such amines with phosphate esters of the formula R_8O-P(O)(OH)-OR_9 and HO-P(O)(OH)-OR_9, wherein R_8 and R_9 are independently C_1 to C_{20} alkyl of alkyl ethoxylate of the formula -alkyl-(OCH_2CH_2); cyclic amines such as imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline, where higher alkyl is from 12 to 22 carbons and lower alkyl is from 1 to 4 carbons, such as described in UK Patent Application GB 2,173,827; and quaternary ammonium compounds of the formula $R_{10}R_{11}R_{12}R_{13}N^+X^-$, wherein R_{10} is alkyl having 8 to 20 carbons, R_{11} is alkyl having 1 to 10 carbons, R_{12} and R_{13} are alkyl having 1 to 4 carbons, preferably methyl, and X is an anion, preferably Cl^- or Br^-, such as C_{12-13} alkyl trimethyl ammonium chloride.

Yet another optional component in laundry bars is a bleach component. The bleaching component can be a source of ^-OOH group, such as sodium perborate monohydrate, sodium perborate tetrahydrate and sodium percarbonate. Sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) is preferred since it has a dual function of both a source of HOOH and a source of sodium carbonat . Another optional bleaching component is a peracid per se, such as a formula:

$$CH_3(CH_2)_w\text{-NH-C(O)-}(CH_2)_zCO_3H$$

wherein z is from 2 to 4 and w is from 4 to 10. The bleaching component can contain, as a bleaching component stabilizer, a chelating agent of polyaminocarboxylic acids, polyaminocarboxylates such as ethylenediaminotetraacetic acid, diethylenetriaminopentaacetic acid, and ethylenediaminodisuccinic acid, and their salts with water-soluble alkali metals. The bleach components can be added to the bar at a level up to 20%, preferably from about 1% to about 10%, more preferably from about 2% to about 6%.

Sodium sulfate is a well-known filler that is typically used in laundry bars. It can be a by-product of surfactant sulfation and sulfonation processes, or it can be added separately. Other filler materials include b ntonite talc and calcium

carbonate (also known as Calcarb).Fillers are typically used at levels up to 40%, preferably from about 5% to about 25%.

Binding agents for holding bars together in a cohesive, soluble form can also be used, and include natural and synthetic starches, gums, thickeners, and mixtures thereof.

Soil suspending agents can be used in laundry bars. Their use is typically balanced with the fabric softening clay/clay flocculating agent combination to provide optimum cleaning and fabric softening performance. Soil suspending agents can also include water-soluble salts of carboxymethylcellulose and carboxyhydroxymethylcellulose. A preferred soil suspending agent is an acrylic/maleic copolymer, commercially available as Sokolan®, from BASF Corp. Other soil suspending agents include polyethylene glycols having a molecular weight of about 400 to 10,000, and ethoxylated mono- and polyamines, and quaternary salts thereof.

Optical brighteners are also preferred optional ingredients in laundry bars. Preferred optical brighteners are diamino stilbene, distyrilbiphenyl-type optical brighteners. Preferred as examples of such brighteners are 4,4'-bis{[4-anilino-6-bis(2-hydoxyethyl) amino-1,3,5-trizin-2-yl]amino}stilbene-2,2'-disulfonic acid disodium salt, 4-4'-bis(2-sulfostyryl) biphenyl and 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl) amino]stilbene-2,2'-disulfonic acid disodium salt. Such optical brighteners, or mixtures thereof, can be used at levels in the bar of from about 0.05% - 1.0%.

Dyes, pigments, germicides, and perfumes can also be added to the bar composition

Processing

The colored particulate compositions of the present invention can be formed by spraying a solution or dispersion of color body (i.e. dye or pigment) onto the particulate carrier, drying the colored particles to a free flowing state, spraying an aqueous solution of dextrin glue onto the dried colored particles, thereby agglomerating said particles and forming a glue coating on said particles, drying the particles to a free flowing state, ageing the particles for at least 1 (typically 1 to 360) hours to harden the coating, spraying the coated particles with additional aqueous glue solution, drying the particles to a free flowing state, thereby forming an additional glue coating on said particles, and ageing the particles for from at least 24 (typically 1 to 720) hours to harden the

coating. After each drying step, the particles are typically screened to isolate preferred particle sizes. In the event a rapidly hydrating material such as sodium tripolyphosphate is used as the carrier particle, a drying step is usually not needed between the color-spraying step and the first glue-spraying step. For the colored carrier particles, a particle size of less than about 1400 microns is preferably isolated and used in the first glue coating step. After drying of particles from the first glue coating, particles of from about 1400 to about 150 microns are preferably isolated and then aged for further use in the process. After the final drying , a particle size of from about 1170 to about 210 microns is preferably isolated for ageing and subsequent use as speckles in detergent products.

In the first step, the solution/dispersion of color body can be sprayed onto the particulate carrier using any suitable apparatus for uniformly spraying liquids onto particulate solids. A particularly suitable apparatus is a rotating drum in which the particulate carrier is agitated while the solution/dispersion of color body is sprayed into the drum. Drying of the colored particles can be carried out in any suitable drying apparatus. Examples of suitable drying apparatus ar concrete mixer, plow shear, V-Blender and Forberg Mixer. Also, fluid bed processes such as the Wurster Process can be used. Drying can be conveniently achieved by continued agitation and exposure to air in the same apparatus used for spraying the dye. Additional drying can be achieved by spreading the particles on pans, and/or storage in a dry place, with exposure to air. Spraying of the first (inner) coating and the second (outer) coating onto the particles can be accomplished in any type of apparatus used for spraying liquids onto particulate solids. The same type of spraying apparatus used for the spraying of color bodies in the first step can be used. Likewise, drying particles after each coating can be accomplished in the same type of apparatus and manner used for drying the particles which have been sprayed with color bodies in the first step.

Ageing of particles after the first and second glue coatings can be carried out in containers such as bags or bins in a dry place. Some additional drying, i.e. evaporation, of free moisture may occur during the ageing process.

Laundry bars containing the colored particulate compositions of the present invention can be processed in conventional soap or detergent bar making equipment with some or all of th following key equipment:

blender/mixer, mill or refining plodder, two- stage vacuum plodder, logo printer/cutter, cooling tunnel and wrapper.

In a typical process the raw materials (surfactant, builder, etc.) are mixed in the blender. The colored particulate compositions are included in this mixing step. The mixing can take from one minute to one hour, with the usual mixing time being from about two to twenty minutes. The blender mix is charged to a surge tank. The product is conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyer.

After milling or preliminary plodding, the product is then conveyed to a double vacuum plodder, operating at high vacuum, e.g. 600 to 740 mm of mercury vacuum, so that entrapped air is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar can be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

Examples of the invention are set forth hereinafter by way of illustration and are not intended to be in any way limiting of the invention.

EXAMPLE I

A batch of blue speckles in accordance with the present invention are prepared as follows:

a. Dye Slurry

Aquasol Blue Dye	1.997 kg
Ultramarine Blue	1.029
Photoactive Bleach (20% aqueous solution)	0.267
Synthetic surfactant granules	0.012
Water	1.580
	4.885 kg

The Aquasol, Ultramarine Blue and surfactant granules are dispersed in 1 kg. water. The photoactive bleach is then added. The remaining 0.580 water is used to wash powders adhering to containers and utensils into the dye slurry. The mixture is sieved through a 35-mesh screen prior to use.

b. Glue Slurry

Dextrin Powder	2.820 kg
Carboxymethylcellulose	0.128

Borax	0.563
Water	5.505
	9.016

The dextrin and carboxymethylcellulose are mixed in a dry basin. The water is heated to at least 71°C in a stainless steel vat. The borax is dissolved in the water and heated to 90°C. The dextrin/carboxymethylcellulose is added to the borax solution and the mixture is cooked in the vat at 88°-93°C for 15 minutes while stirring gently. The mixture is allowed to stand until froth disappears, and then is sieved through 35-mesh screen and allowed to age for 20-48 hours prior to use.

c. Carrier Particles

Dense Soda Ash	49.605 kg

d. Spraying Equipment

i. Air compressor providing 20-60 psi
Energair Single Phase Industrial Motor, 5 hp
cfm 28
voltage 220 single phase
amp. 23
RPM 3470

ii. Spray gun
Sprayet (Thomas Industries)
For dye slurry use outer nozzle size 3.0mm and inner nozzle size 2.0mm.
For glue slurry use outer nozzle size 3.5mm and inner nozzle size 3.0mm

iii. Mixer
Ramrod brand
hp. 2-3
Capacity 1 bag cement
Speed adjusted to maintain 30-40 rpm

e. Procedure

The soda ash is loaded into the mixer and th dye slurry is sprayed onto the soda ash during a 10-15 minute period while the mixer is rotating. Rotation of the mixer is continued for another 10 minutes until the particles are dry and free flowing, Then, while continuing rotation of the mixer , 6.01 kg of glue slurry (at 60°±6°C) is sprayed onto the particles over a period of from 10-15 minutes. Rotation is continued until the particles are dry and free flowing.

The particles are then sieved on a 12 mesh screen, and any lumps are rubbed onto the screen to reduce them to 12 mesh or less.

The sieved particles are spread on pans at ambient temperature for about 30 minutes, then transferred to bags for aging for about 48 hours, then re-sieved on a 14 mesh screen.

The particles are then loaded into the mixer and 3 kg of glue slurry, at 60°±6°C are sprayed onto the particles over a period of 4-7 minutes. Rotation of the mixer is then continued for at least about 10 minutes until the particles are dry and free flowing. The particles are sieved on a 12 mesh screen and lumps are broken up by rubbing them onto the screen. The particles are then spread on pans at ambient temperature for about 30 minutes, after which they are transferred to bags for 72 hours aging, after which they are sieved, and th fractions passing through 14 mesh and remaining on 65 mesh are used for speckling of detergent bars

EXAMPLE II

A synthetic laundry bar of the present invention, having the following composition is prepared by conventional blending, milling and plodding procedures, with the speckles of Example I being added in the, blending step. The bar has a pleasing appearance, with sharply defined blue speckles on a white background.

Component	% Weight
Na coconut alcohol sulfate	15.750
Na linear alkylbenzene sulfonate	6.750
Coconut fatty alcohol	1.470
Na tripolyphosphate	11.600
Na carbonate	15.000
Na sulfate	8.904

Ca carbonate	28.321
Zeolite	0.975
Glycerine	1.000
Diethylenetriaminepentaacetate	0.500
Polyvinylpyrollidone N-oxide	.140
Sokolan CP-5 (soil suspending agent)	0.400
Carboxymethylcellulose	0.360
Soil release polymer	0.200
Optical brighteners	0.200
Titanium dioxide	1.000
Speckles of Example I	4.00
Perfume	0.500
Moisture & Misc.	2.930
TOTAL	100.000

The bar has a white background with distinct, non-smeary blue speckl s distributed evenly throughout.

WHAT IS CLAIMED IS:

1. A colored particulate composition suitable for use in cleaning products, said particulate composition comprising,
   a) from about 50% to about 95% of a particulate carrier material,
   b) from about 1% to about 30% of color body,
   c) from about 1% to about 40% dextrin, in the form of dextrin glue, wherein the dextrin is present on a particle comprising the carrier and color body in two discrete coatings, the inner coating comprising from about 5% to about 85% of the total amount of dextrin, and the outer coating comprising the remainder of the dextrin, and
   d) from about 0.3% to about 35% moisture.

2. The composition of claim 1, wherein the amount of particulate carrier is from about 70% to about 85%.

3. The composition of claim 2 wherein the amount of dextrin is from about 5% to about 15% and wherein the inner coating comprises from about 30% to about 70% of the total amount of dextrin and the outer coating comprises the remainder of the dextrin.

4. The composition of any of claims 1 through 3 wherein the particulate carrier particle is a hydratable material.

5. The composition of claim 4 wherein the hydratable salt is selected from the group consisting of sodium sulfate, sodium carbonate and sodium tripolyphosphate.

6. A laundry bar composition comprising,
   a) from about 4% to about 30% anionic synthetic surfactant,
   b) from about 5% to about 50% detergency builder, and
   c) from about 0.01% to about 15% colored particulate composition of Claim 1, wherein the color of said particulate composition contrasts with the background color of said laundry bar.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/16404

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/40 C11D17/00 C09B67/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 1 327 635 A (PROCTER & GAMBLE) 4 September 1963 see claims; examples ---	1-7
A	US 4 097 418 A (ROLFES THOMAS RICHARD) 27 June 1978 see column 1, line 63 - column 2, line 32; claims; examples ---	1-5,7
A	EP 0 060 728 A (UNILEVER) 22 September 1982 see the whole document ---	1-5,7
A	GB 1 064 414 A (PROCTER & GAMBLE) 5 April 1967 see the whole document --- -/--	6

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 June 1997	23/06/97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Grittern, A

Form PCT/ISA/210 (second sheet) (July 1992)

7. A process for preparing a colored particulate composition suitable for use in detergent products, said process comprising the steps of;
   a) spraying an aqueous solution or dispersion of a color body onto a particulate carrier material having a particle size of from about 45 to about 1600 microns,
   b) drying the particles from Step a),
   c) spraying onto the dried particles from Step b) an aqueous solution of dextrin in the form a glue, thereby agglomerating said particles and forming a coating thereon,
   d) drying the coated particles from Step c),
   e) ageing the particles from Step d) for at least about one hour,
   f) spraying onto the particles of Step e) an aqueous solution of dextrin in the form of glue, thereby forming a second coating of glue on said particles,
   g) drying the particles of Step f), and
   h) ageing the particles from Step g)

8. A process for preparing a colored particulate composition suitable for use in detergent products, said process comprising the steps of;
   a) spraying an aqueous solution or dispersion of a color body onto anhydrous sodium tripolyphosphate having a particle size of from about 45 to about 1600 microns,
   b) spraying onto the dried particles from Step a) an aqueous solution of dextrin in the form a glue, thereby agglomerating said particles and forming a coating thereon,
   c) drying the coated particles from Step b),
   d) ageing the particles from Step c) for at least about one hour,
   e) spraying onto the particles of Step d) an aqueous solution of dextrin in the form of glue, thereby forming a second coating of glue on said particles,
   f) drying the particles of Step e), and
   g) ageing the particles from Step f)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 333 270 A (PROCTER & GAMBLE) 20 September 1989 see claims	1,7
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Information on patent family members

I· ational Application No
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